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Membranes for Gas Separation Current Development and Challenges

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Abstract—A new bang of natural gas demand has opened up the opportunities towards the utilization of membrane technology for the purification process.The advantages in terms of smaller footprint, lower weight, minimum utility requirement and low labor intensity make them appropriate for wide scale applications. Polymeric membrane is one of the greatest emerging fields in membrane material development. Nevertheless, the separation performance of the existing polymeric materials were reached a limit in the trade-off between permeability and selectivity. The development of inorganic material gives a significance improvement in membrane performance but it outrageously expensive for many applications and having complicated procedure during fabrication process have limit the application of inorganic membrane in gas separation. Thus, a rapid demand in membrane technology for gas separation and the effort toward seeking the membranes with higher permeability and selectivity has motivated the development of mixed matrix membrane. Mixed matrix membrane (MMM) which incorporating inorganic fillers in a polymer matrix is expected to overcome the limitations of the polymeric and inorganic membranes. Apart from an overview of the different membrane materials for gas separation, this paper also highlights the development of mixed matrix membrane and challenges in fabrication of mixed matrix membranes.

Introduction

Natural gas is one of the important constituents of the world's supply of energy and the demand for natural gas is increasing rapidly [1]. Natural gas has been forecasted to be the quickest growing fuel of world energy consumption. The utilization of natural gas is predicted to rise by an average of 2.3 % annually from 2001 to 2025. Natural gas consumption is estimated to be 151 trillion cubic feet by year 2025, which is 70 % higher than the amount of natural gas consumed in 2001 [2].

Natural gas mostly consists of methane and several gases such as ethane, propane, butane, heavy hydrocarbons and other impurities like hydrogen sulphide, carbon dioxide and nitrogen. Some rare gases and metals, including mercury and helium might be traced as a part of the natural gas [3]. Practically, the impurities such as CO_2, H_2S and heavy molecular weight hydrocarbons must be removed from natural gas because it will decrease the heating value of natural gas, generate corrosion problem to the pipelines and equipments and contribute to the atmospheric pollution [4].

The current technologies used to purify natural gas include absorption, adsorption, cryogenic and membrane separation [5].Comparing with other natural gas separation techniques, membrane process is one of the most appropriate technology to separate bulk CO_2 and impurities from natural gas under offshore operating condition. This technology demonstrates the advantages in terms of modular installation, smaller footprint, lower weight, easier maintenance and low labour intensity [6].

As the market demand for membrane separation technology increases, a membrane that having greater permeability and selectivity compared to the existing membranes is desired. A good membrane material should demonstrate high separation performance and good mechanical strength.

Membranes can be fabricated and synthesized using different materials; organic to inorganic, depending on their purposes. Even though the polymeric membranes have been widely used, its separation performance reached a limit in the trade-off between permeability and selectivity as represented by Robeson plot [7]. Meanwhile, inorganic membranes give higher permeability and

selectivity compared to polymeric membrane, but this type of membrane is not easy to fabricate and outrageously expensive for many applications [8].

Therefore, a potential approach to improve the separation properties of membranes by incorporating dispersed solids such as zeolites and carbon molecular sieves into the polymeric matrix is developed.The resultant membrane combines the advantages of polymeric and inorganic materials, including economical capabilities of polymers and high separation properties of inorganic fillers.

Membrane Materials for Gas Separation

Polymeric Membranes. Most commercial and research works focus on the utilization of polymeric materials to fabricate gas separation membranes since it exhibited reproducibility for large scale production and low cost of fabrication compared to inorganic membrane[9]. Polymeric membranes achieve separation from a different mechanism based on its property of material and structural morphology [10]. Polymeric membranes used in gas separation are mainly fabricated using polyimide, cellulose acetate and polysulfone etc [11].

High permeability and high selectivity in gas separation are the criteria for an attractive polymer material. Polymeric membranes are robust and proficient to endure mechanical harsh operation. Beside of its advantages in separation, this type of membrane is capable to form asymmetric hollow fibers that give high surface area and economically viable [12, 13]. Polymeric membranes have been broadly used in the purification of natural gas and separation of H_2 from refinery purge gas.

Polymeric membranes can be classified into two categories; i) size-selective and ii) sorption-selective [14]. The first type of membrane material is glassy polymer which consists of stiff chain and lower free volume that stringently separates based on size of the components and it favors small molecule to pass through the membrane. While, the second type of membrane is highly flexible, rubbery and has high free volume that separates the component based on condensability where it prefers to separate larger components[13].

Among the polymeric materials, polypyrrolone and polyimide have the greatest transport performance[12]. Although the polymeric membrane gives a good performance in separation, they are still limited by an upper bound of the permeability and selectivity in which the permeability increases when the selectivity decreases and vice versa as illustrated in Robeson plot in Fig.1 [15].

Besides, polymeric membranes often facing limitation such as plasticization and aging, which affect the separation performance of the membrane [16]. Plasticization occurs when the free chain of polymer tends to loose in order to give a space for penetrant to permeate and thus, increases the number of hypothetical gaps and free volume available within the membrane matrix. On the other hand, physical aging is a process which the performance of membrane deteriorates with time. Thus, the shortcomings of these materials prompt the researchers to find an alternative membranes in order to enhance the gas separation performance.

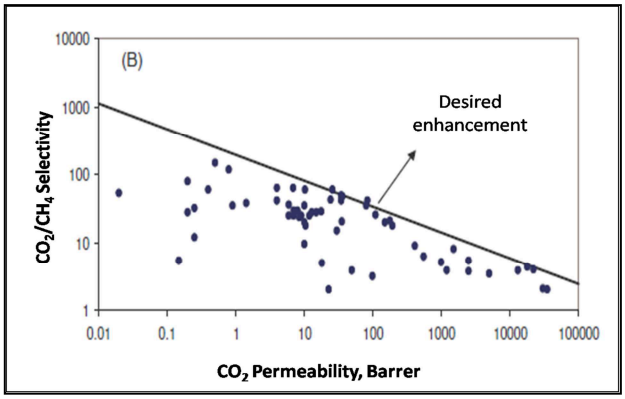

Fig 1: Upper bound limit for CO_2/CH_4 separation by various type of polymeric materials [15]

Inorganic Membranes. Inorganic membranes are developed to cater the drawbacks of polymeric membranes. These materials normally gives a good performance with high thermal resistance and high stability. Similar to polymeric membrane, inorganic membrane can be fabricated into dense (e.g: palladium, silver, zirconia and nickel membrane) and porous membrane (e.g: alumina, silica, zeolite) [17]. However, most of the researches focused on porous inorganic membrane rather than dense membrane due to low flux or permeability of the dense membrane.

Carbon molecular sieve (CMS) and zeolite membranes are the examples of inorganic membrane that gives great performance in terms of permeability and selectivity. Carbon membrane can be formed by a pyrolisis of thermosetting polymeric precursor at high temperature [18].

Zeolite membrane is normally fabricated using in-situ hydrothermal synthesis onto the porous stainless steel, α-alumina or γ-alumina discs [19]. Zeolite membranes such as SAPO-34, ZSM-5, Y-type, silicate A-type and silicate p-type have been synthesized on porous support for gas separation. These supported membranes have a thin zeolite separation layer with the porous support in order to provide mechanical strength to the membrane.

However, inorganic membrane is difficult to fabricate and extremely expensive. It is anticipated that a zeolite membrane module costs US$ 3000/m^2compared to US$20/$m^2$ for the polymeric hollow fiber membrane modules [20]. Therefore, industrial application of inorganic membrane is restricted due to the high cost of production, lack of technology and knowledge in handling the issues of brittleness of inorganic membrane as well as difficulties in producing defect free membrane.

Mixed Matrix Membrane (MMM). The restrictions of polymeric and inorganic membranes encourage the researchers to seek for a membrane material that demonstrating higher permeability and selectivity for a wide scale application especially for gas separation. Selective inorganic fillers such as zeolites are integrated into the polymer matrix to form MMM in order to achieve higher permeability and selectivity. The suitable selection of polymer matrix, inorganic filler and the elimination of interfacial defects are an important key to develop a defects-free MMM.

Development of Mixed Matrix Membrane

In early study of MMM, it has been found that most of the researchers utilized rubbery polymer as polymer matrix in the fabrication of MMM. In 1970s, a delayed in diffusion time lag for CO_2 and CH_4 permeability was found by Paul and Kemp [21] in MMM consists of zeolite 5A and polydimethylsiloxane (PDMS). Jia et al. [22] also discovered that the incorporation of 70wt% of silicate in PDMS has increased the selectivity of CO_2/CH_4 from 3.42 to 8.86.

Duval et al. [23] have reported the fabrication of a series of MMMs containing different types of inorganic fillers and polymer matrix for CO_2/CH_4 separation. They incorporated zeolites (silicate-1, 13X, KY and 5A) and carbon molecular sieves (W20, Cecalite, Carbosieve) in PDMS, polychloroprene (PCP), nitrile butadiene rubber (NBR 45 and NBR 50) and ethylene-propylene rubber (EPDM). Based on their studied, they observed that nonselective voids appeared as loading of zeolites increases. NBR 45 incorporated with 45% of Zeolite KY showed higher CO_2 permeability and CO_2/CH_4 selectivity of 14 Barrers and 35, respectively. While, by incorporating 50 wt% of Carbosieve in EPDM, the permeability of CO_2 has been increased from 81 to 120 Barrer and the CO_2/CH_4 selectivity increases from 4.3 to 8.

As the performance of MMM fabricated using rubbery polymer is still far below the upper bound limit in Robeson plot, the development in mixed matrix membrane was continued by utilizing glassy polymer as a polymer matrix. Kulprathipanja et al. [24] reported that the incorporation of 25wt% silicalite into cellulose acetate (CA) increases the selectivity of CO_2/H_2 from 0.7 to 9.6. Suer et al. [25] discovered the increment of CO_2/N_2 selectivity from 3.7 to 4.4 when zeolite 4A and 13X incorporated in polyethersulfone (PES).

To date, various researchers still facing the difficulties in obtaining defects free mixed matrix membrane. Mahajan et. al [26] discovered that the gas permeabilities were not affected using zeolite 4A-Matrimid MMM. Same problem was observed by Gur [27] during the preparation of MMM using zeolite 13X and polysulfone (PSU). This was mainly due to a poor adhesion between glassy

polymer and zeolite. Vankelecom et al. [28] also discovered that unsatisfactory polymer-filler adhesion was observed when silicate, borosilicate and zeolite Y incorporated into polyimide matrix.

Challenges in Mixed Matrix Membrane Fabrication

The major challenges in the MMM fabrication is the dispersibility of inorganic particles in the polymer phase [29]. Improper dispersion may result towards the agglomeration and sedimentation of inorganic filler in the resultant MMM. Physical properties and density difference between inorganic filler and polymer matrix contribute to the formation of heterogeneous phase in the membrane. This condition should be avoided because it causes the pinholes, non-selective defects and thus, destroy the mechanical stability of membrane particularly when dealing with high loading of inorganic filler.

Compatibility between inorganic filler and polymer phase plays an important role in MMM fabrication [30].The combination of these materials will determine the resistance ratio to the gas transport and therefore affects the performance of the membrane.

Besides, the particles size of the inorganic filler in MMM fabrication is vital in producing high quality MMM. The previous studies mainly utilized micron size of inorganic filler for MMM fabrication. As reported by Ersolmaz et al. [31], smaller particles offer higher polymer/particle interfacial area, enable to produce a thinner MMM as well as to provide better opportunity to disrupt polymer chain packing and improve molecular transport.

Another critical challenges in MMM fabrication is to achieve a proper interfacial contact between the inorganic particle and polymer phase[32]. Poor interfacial contact causes the formation of interface voids and affects the amount of inorganic filler loading in MMM. Duval [33] and Vankelecom [28] found that the interface voids occurred in MMM were mainly due to high stress during solvent evaporation step, inflexibility of polymer chain, repulsive force and dissimilar thermal expansion coefficient between inorganic filler and polymer phases [34].

Conclusion

This paper provides a comprehensive review on the membrane materials for gas separation including, polymeric, inorganic and mixed matrix membranes. The development of these membrane materials as well as the associated problems are discussed.

The gas separation performance of polymeric membrane is limited by Robeson upper bound, whereas inorganic membranes are not favorable due to its high manufacturing cost and difficult to fabricate. Thus, mixed matrix membranes which embed inorganic materials in polymer matrix are developed to overcome these weaknesses. An appropriate combination of inorganic filler and polymer in MMM fabrication could resulted in high quality MMM with minimum defects and therefore, enhance the gas separation performance which could exceed the Robeson's upper bound limit. Thus, future research and effort on MMM's development is worthy to be explored in order to developed a promising generation of membrane materials for gas separation application.

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